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3D Carbon Nanotube Networks as Mechanical, Electrical and Photovoltaic Transducer and Superhydrophobic Filter

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14. ABSTRACT
This team synthesized 3d-networks of curved and interconnected carbon nanotube structures by addition of sulfur during synthesis, and this material was subjected to assessment of its elasticity, oleophilic/toxic agent absorption, and hydrophobicity. The production process seems to introduce a marked variability in the CNT diameter, which creates a porous network, the physical structure of which lends itself to lipophilic and hydrophobic properties. Additionally, a cut piece of the sample was evaluated for photoelectric conversion and as a working electrode in a standard electrochemical cell, showing good properties for both applications.

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Abstract

In this project we have demonstrated that is possible to synthesize three-dimensional networks consisting of curved and interconnected nanostructures mainly composed of carbon nanotubes (CNTs) by adding sulfur, to enhancing the growth, during the synthesis process. Studies on the microscopic structure indicate that the material presents a marked variability in the CNT diameter and carbon fibers can be found in the network. We have investigated the relationship between the microscopic properties of the structure and some applications that we tested. In particular, we have shown that the porous nature of the network is directly responsible of the hydrophobic and the lipophilic properties. Besides, we have used a cut piece of the sample, which possesses a self-sustainable structure as a working electrode in standard electrochemical cell. Thus proving the capability of the system to respond to incident light and generate a photocurrent in the visible and near ultraviolet region.

Development of the work:

The project of our research Unit has been developed as follows:

a) synthesis, structural and electronic investigation of multi wall carbon nanotubes by using a new apparatus operating in our laboratory and reported in Fig.1.

b) Carbon nanotube sponges have been characterized by electrical and mechanical (stress, strain and shear) measurements to assess their elasticity, oleophilic and toxic agents absorption properties and fully hydrophobicity.

c) production of samples of large size (5cm x 5cm) of samples as prototypes for water filtration and sensors.

The achievements of the above objectives entails the characterization of carbon nanostructures by using different morphological, structural, electronic and optical techniques. This has been obtained through a CVD (Chemical Vapor Deposition) fabrication of carbon nanotubes by mixing several gases containing acetylene, ferrocene, thiophene and argon with proper concentration and temperature.

d) The CNT have been characterized by structural, electronic, mechanical and transport properties. These characterizations have been achieved by using electron spectroscopies and microscopies (SEM, TEM, EELS, XPS, Raman) to assess the repeatability and elastic properties of the structure.

The research personnel involved has been:

Prof.Maurizio De Crescenzi (full professor of Structure of matter) at Roma Tor Vergata University

Dr.Manuela Scarselli, Researcher (permanent position) at Roma Tor Vergata University

Dr.Paola Castrucci, Researcher (permanent position) at Roma Tor Vergata University

Dr.Francesco De Nicola, PhD student at Roma Tor Vergata University

The group has been in the past awarded with a grant from EOARD (2011) (FA8655-11-1-3036) on the development of electrochemical solar cells based on carbon nanotubes decorated by metallic nanoparticles. The present research has been presented at a number of International conference on nanostructures and renewable energies and it has been the subject of more than ten publications on international reviews with the acknowledgement of EOARD for financial support.

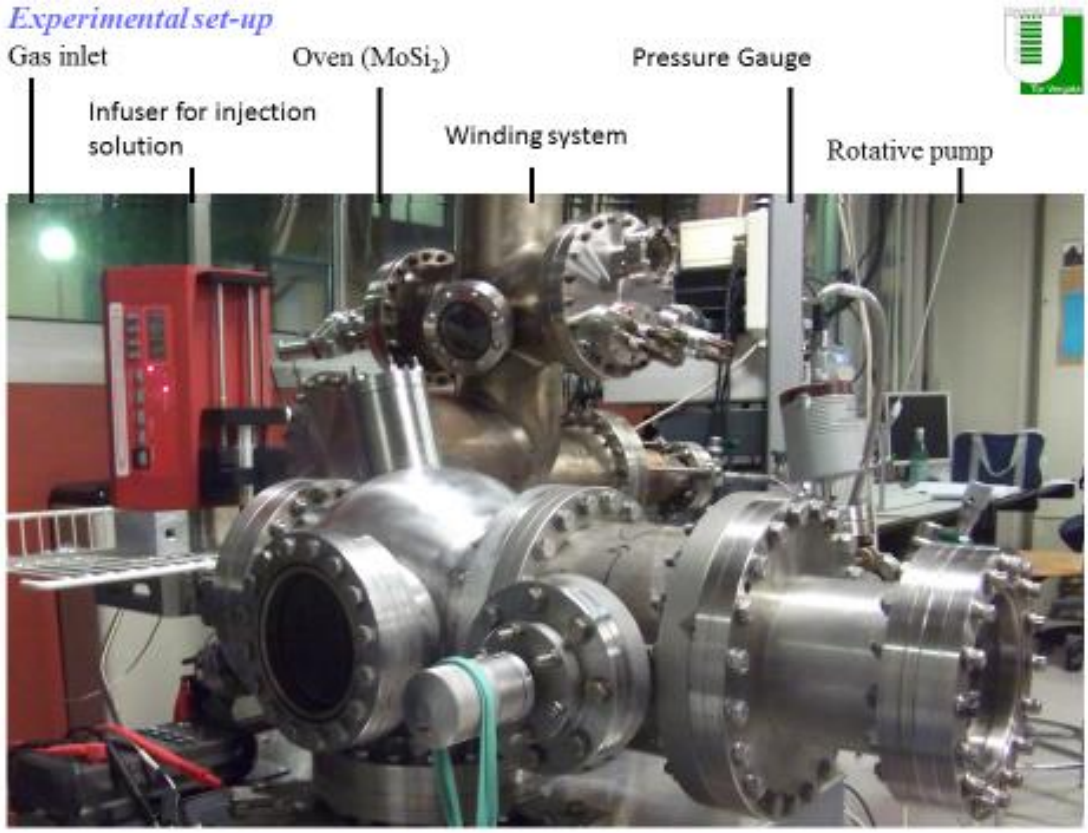

Figure 1. Experimental set up, operating at Roma Tor Vergata University, to synthesize 3D carbon nanotubes sponges by using a modified CVD process in which acetylene, ferrocene, thiophene and argon are mixed passing through an oven at high temperature.

Objectives, approach and results

In the last years, there has been growing interest in developing natural and synthetic three-dimensional architectures rather than two-dimensional ones because of the increase of active surface area throughout the entire 3D structure. Hydrogels, organogels, and aerogels based on silica [1] or

carbon [2] and consisting of micro, and macroscopic assemblies are reported in the literature. In particular, self-sustaining assemblies that show high porosity [3], structural stability, and good electrical conductivity [4] are the best candidates for environmental applications such as filtration [5], separation [6], biological sensors [7], and oil spill remediation [8] but also as mechanical actuators [9], catalytic supports [10], and super capacitors [11]. In this research field, CNTs based architectures are the focus of intense research activity [2], since CNTs are one-dimensional structures with well-known electrical and mechanical properties, they are the ideal building blocks for constructing three-dimensional random meshes from their overlapping.

In this project we have shown that following a CVD synthesis from different precursors, it is possible to directly synthesize three dimensional carbon networks consisting of random interconnected nanostructures. The pristine CNT sponges are super-hydrophobic (i.e., a water contact angle greater than 150°) and oleophilic. These features are tested by adsorbing and removing different types of oil from water biphasic systems. Moreover, the bulk carbon nanostructures display a structural flexibility that was rarely observed in other high-porosity materials (e.g. bulk carbon aerogels) or aligned CNT arrays [3]. In addition, to test the capability of the system to respond to incident light and generate a photocurrent, we cut a piece of the CNT-sponge, which has a self-sustainable structure, and used it as a working electrode in standard electrochemical cell. In this manner, it was possible to register a good photo-response of the CNT-network to the visible and near ultraviolet range.

The CNT-sponges obtained from the synthesis process described in the experimental section, are light and porous, and can be cut into pieces of the desired size, as shown in Fig. 2. The micro-porosity of the synthesized material causes its lightweight with a density of about 15 mg/cm and good conductivity (electrical resistance of about 40 Ω cm).

Figure 2. Optical image of a box containing CNT-sponges, and a two cut pieces of few cubic mm.

Scanning electron microscopy (SEM) analysis of the inside area of the samples, reveals that the material is made of random self-assembled, long and interconnected tubular nanostructures, with pore sizes from several nanometers to a few micrometers, Fig. 2a. The high number of interconnections is

caused by the bent geometry of the nanostructures induced by the formation of topological defects in the carbon s-p lattice during the growth process. It has been demonstrated that the defects are induced by sulfur addition during the synthesis process, which is known to favor the formation of pentagon and heptagon carbon rings. No structural differences are observed along the whole sample within this morphological characterization.

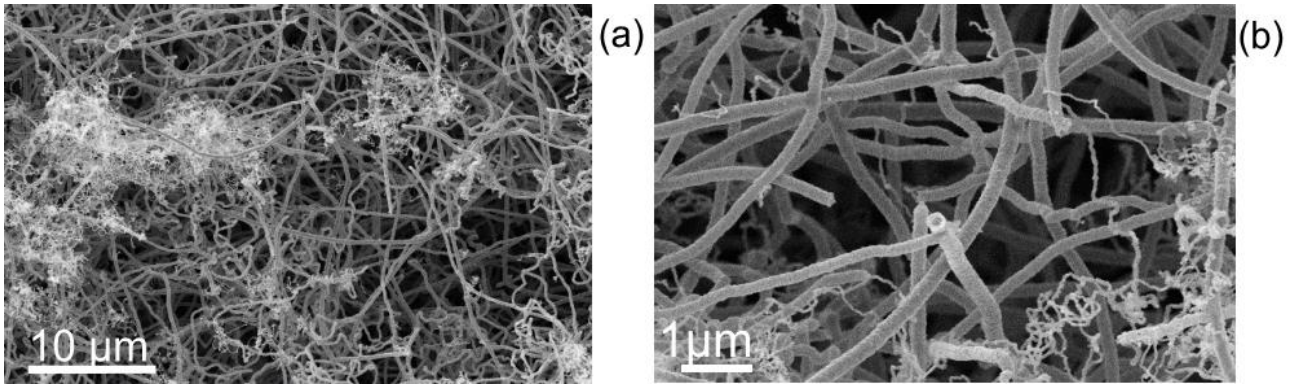

Figure 2. SEM images of the inner structure of the network obtained at two different magnifications (a,b).

The length of the tubes can vary substantially from few nanometers to millimeters, and the CNTs have a high number of walls as evidenced by a transmission electron microscopy study (data not shown). Nevertheless most of the tubes are not capped, see Fig. 2b. Sulfur addition during the growth process is also responsible for inducing a variety of different CNT morphologies such as stacked-cone, bamboo-like and nanofiber with disordered sp hybridized carbon layers. The predominance of C-sp hybridization forms in the nanotubes, as pointed by the electron microscopy studies is further supported by the electron energy loss spectroscopy analysis performed in reflection mode. The energy loss spectrum shows the π and $\sigma+\pi$ plasmons, a characteristic features of the sp lattice. These peaks are located at 6 eV and 24.5 eV respectively, and are downshifted in energy loss with respect to those of highly oriented pyrolytic graphite (7 eV and 28 eV, respectively). This is due to the low dimensionality of the system, as already found for multi-walled CNTs [12].

The micro-porosity of the synthesized material causes its lightweight and the capability to sustain high compression loads as recently reported for our samples [13]. Two interesting properties that originate from the high porosity and the presence of highly interconnected one-dimensional nanostructures are the hydrophobicity and olephilicity. To better characterize the hydrophobicity one can measure the advanced static contact angle at room temperature for water droplets of different volumes ranging from 5 µL to 20 µL, as shown in Fig.3a.

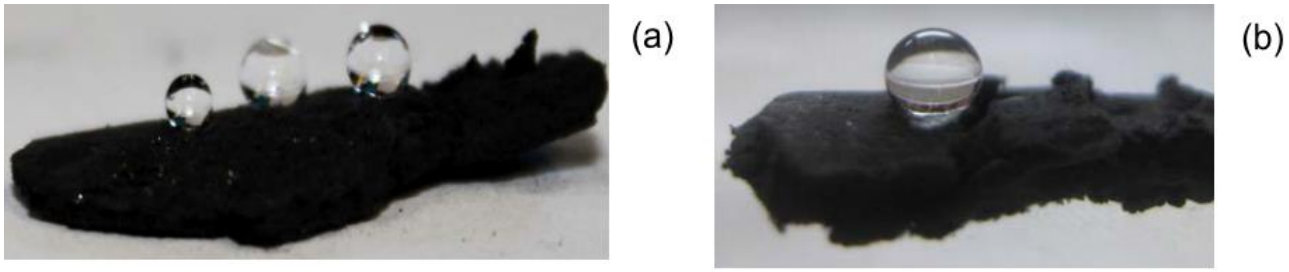

Figure 3. Optical images (a) and contact angle profile (b) of water droplet of different volume on the bulk material.

The presence of a composite solid-liquid air interface explains the high value of the measured contact angle (= 175°), as evaluated in Fig. 3b, with no observable roll-off angle, even when the substrate is turn upside down, see Fig. 4a. Therefore, we infer that the contact angle hysteresis is so high to pin the water droplet on the MWCNT surface.

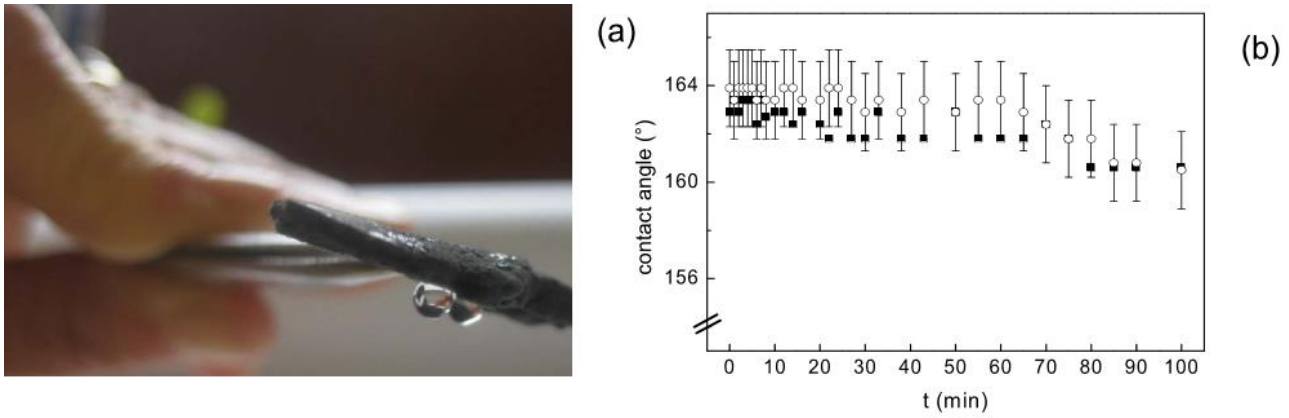

Figure 4. Stability of the super-hydrophic state. No roll-off angle has been measured, even when the substrate is turn upside down (a). Variation of the measured contact angle for a 10 µL water droplet for two different samples, the vertical scale has been expanded for better view (b).

The stability of the super-hydrophobic state can also be inferred from the measurement of the static contact angle variation as a function of time at room temperature, Figure 4b. A reduction of less than 2% of the initial value is measured after 100 minutes that can be attributed to water evaporation. These findings indicate that the CNT-sponge wettability is well described by a Cassie- Baxter model for which a quite rough surface allows air trapping and ensures the high contact angle found. In particular, in such a system pores in the random network (i.e., void fraction) favor air trapping owing to the strong capillary force that the surface exerts on the liquid.

On the other hand, the CNT-sponge shows a high absorption capacity towards oils (vegetal, engine and similar others) since the contact angle is remarkably less than 90°, therefore it is lipophilic [14]. Figure 6a, shows an optical image of the starting of the removal of engine oil (from AGIP company,

ISO46) spreading on the water surface using the as-prepared three-dimensional material. In particular, a CNT sponge of 1.5 mg is able to selectively uptake vegetable oil up to 150 times of its initial weight. The absorption capacity is defined as the ratio between the final and initial weight after full absorption [5]. The observed high value of the uptake efficiency can be ascribed to the presence of both (i) carbon sp species (e.g. nano-fibers), characterized by a rough surface, and (ii) the high porosity. It is in fact known that irregular surfaces make adsorption of organics much easier than smooth ones [15]. Once the CNT-sponge becomes saturated, the absorbed oil can easily be removed by mechanically squeezing it. Alternatively, igniting the sponge can eliminate the oil, as well. In the latter case, as soon as all the oil is burnt away, the fire blows over without destroying the sponge, (Fig. 5b), which is hence ready to be reused. We investigated with SEM on the nanostructure properties before and after oil absorption and subsequent burning process. In particular, Fig. 5c was obtained after two absorption- burning processes on the surface of the CNT sponge. While the porous assembly appears almost entirely preserved the nanostructures composing the network are partially covered by some oil residues.

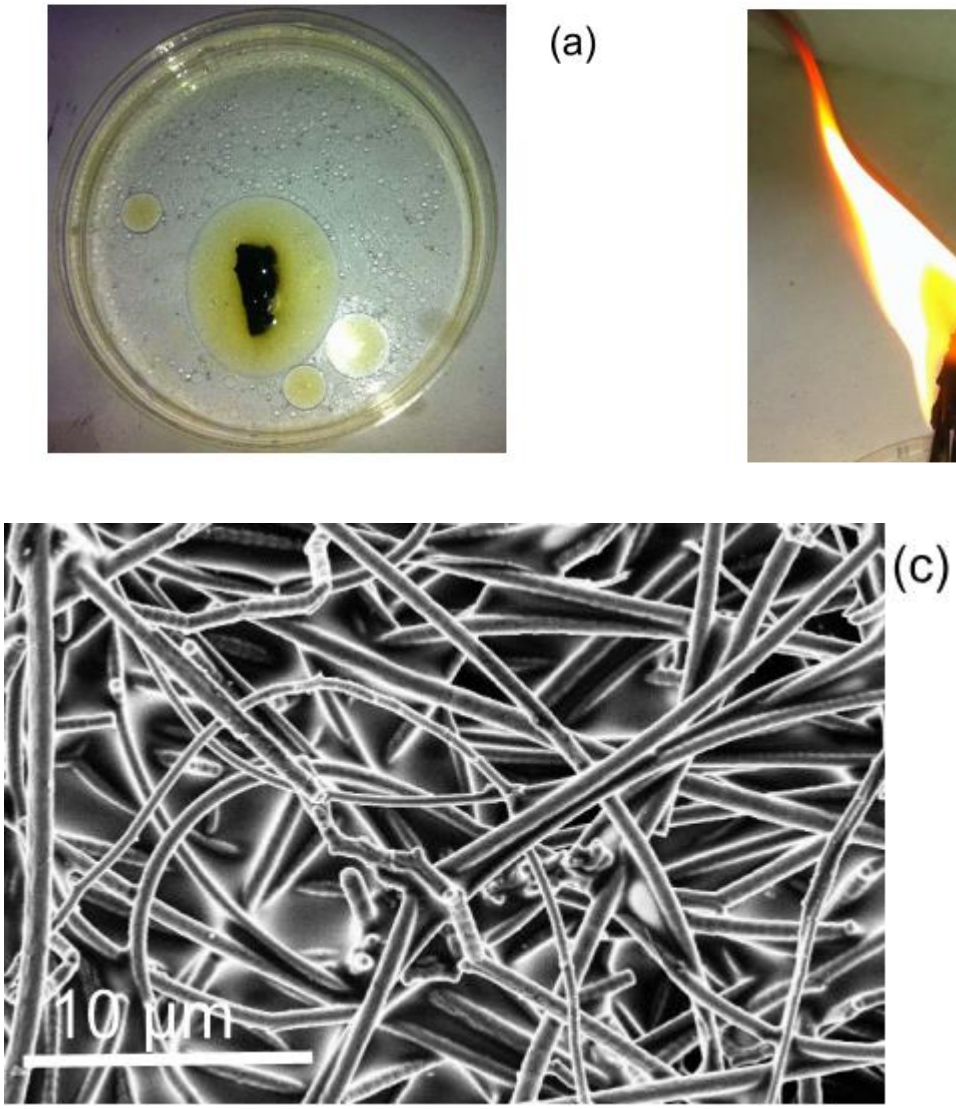

Figure 5. Burning and reuse of the CNT sponge. Optical image of the oil-water absorption process (a), and burning after the sponge got saturated (b). SEM image of the CNT- sponge surface after

burning it (c). Fig.4 Due to the Fe nanoparticles embedded into the CNT structure, the 3D network can be directed on water surface to absorb oil up to 150 times of its weight and it can be burnt easily at 1000 K to restart newly the absorption process.

The CNT sponge was directly transferred onto a conductive substrate to make a counter electrode (CE), exploiting its good electrical and mechanical properties. A photoelectric conversion efficiency of about 6.2% has been achieved for the DSC with a CNT-sponge CE, compared with the 7.6% of that with Pt CEs. Recently, our research group showed that 2D films made of MWCNTs only can be used as optical active medium for light energy conversion in a solar cell device [16]. Similarly, we performed a similar measurement using a piece of CNT-sponge, which possesses a self- sustainable structure, as a working electrode in standard electrochemical cell. The photo-response was measured as a function of the incident photon wavelength and expressed in terms of quantum efficiency (IPCE) [16], as reported in Figure 6. In the same figure the response obtained from a MWCNT film grown on a silicon substrate [16] is reported for comparison. The samples show a photo-response in incident photon wavelength range studied with similar IPCE trend. It is interest to notice that the signal coming from the CNT- sponge has maximum around 420 nm, red-shifted with respect to that obtained from the sample made of CNTs only at 360 nm. This difference can be ascribed to the microscopic structure between the sponge-framework and the more homogeneous MWCNT film. Indeed, not only the CNT-sponge presents a marked variability in the tube diameter but also carbon fibers can be found in the network. These structural fluctuations are expected to give different response to incident light.

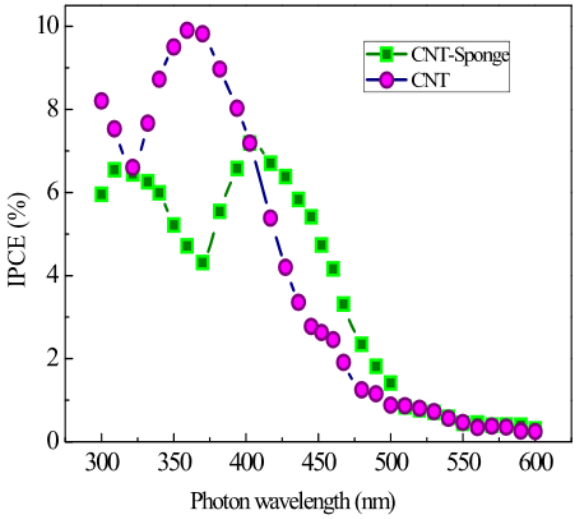

Figure 6. Incident photon-to-current efficiency (IPCE, %) obtained from a MWCNT 2D film (purple circles), and for a CNT-sponge sample (green squares) as function of incident photon wavelength.

Experimental

Chemical vapor deposition process for the growth of 3D CNT networks: The chemical vapor deposition process is carried out in a horizontal hot-wall quartz furnace. Prior to start the growth, the furnace is pumped out to remove air (10 Torr) and then nitrogen is fluxed to restore an ambient inert

pressure (760 Torr). Ferrocene (2.3%wt) and tiophene (1.5%wt), respectively used as catalyst and sulfur precursors, are dissolved in ethanol. The solution is placed in a 10 ml glass syringe and injected into the growth chamber at a constant rate of 7 ml/h through a flux of argon and acetylene (500/200 sccm) which act as gas carrier and carbon precursor, respectively. The vaporized solution and the gas mixture are injected via a stainless tube directly into the high temperature region of the quartz tube furnace. The CNT synthesis is carried out at a temperature of 900-1000 °C, measured by an optical pyrometer. Sulfur addition disturbs the aligned growth while allows for the synthesis of randomly interconnected CNTs with a growth rate along the thickness direction of 4-5 mm per hour.

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2) "Exploiting the hierarchical morphology of single-walled and multi-walled carbon nanotube films for highly hydrophobic coatings" Francesco De Nicola, Paola Castrucci, Manuela Scarselli, Francesca Nanni, Ilaria Cacciotti and Maurizio De Crescenzi, Beilstein Journal of Nanotechnology 6, 353-360 (2015).

3) "Super-hydrophobic multi-walled carbon nanotube coatings for stainless steel" Francesco De Nicola , Paola Castrucci , Manuela Scarselli, Francesca Nanni , Ilaria Cacciotti and Maurizio De Crescenzi, Nanotechnology 26, 145701-6 (2015)

4) "Multi-Fractal Hierarchy of Single-Walled Carbon Nanotube Hydrophobic Coatings" Francesco De Nicola , Paola Castrucci , Manuela Scarselli , Francesca Nanni , Ilaria Cacciotti & Maurizio De Crescenzi, SCIENTIFIC REPORTS | 5 : 8583 | DOI: 10.1038/srep08583

5) "A three-dimensional carbon nanotube network for water treatment" L Camilli , C Pisani , E Gautron , M Scarselli , P Castrucci , F D'Orazio , M Passacantando , D Moscone and M De Crescenzi Nanotechnology 25 (2014) 065701 (7pp) doi:10.1088/0957-4484/25/6/065701

6) "Controlling the Thickness of Carbon Nanotube Random Network Films by the Estimation of the Absorption Coefficient" Francesco De Nicola , Chiara Pintossi , Francesca Nanni , Ilaria Cacciotti , Manuela Scarselli , Giovanni Drera , Stefania Pagliara , Luigi Sangaletti , Maurizio De Crescenzi , Paola Castrucci, Carbon (2015) submitted

7) "3D carbon nanotube scaffolds weave neurites re-growth: bio-hybrid microsystems reconnecting spinal explants in vitro" Sadaf Usmani, Alessandra Fabbro, Manuela Medelin, Jummi Laishram, Denis Scaini, Federica B. Rosselli, Alessio Ansuini, Davide Zoccolan, Emily R. Aurand, Manuela Scarselli, Maurizio De Crescenzi, Susanna Bosi, Maurizio Prato & Laura Ballerini, submitted to Scientific Reports (Nature Group) 2015.

8) "Two-dimensional Wenzel-Cassie-Baxter model for hierarchical surfaces" Francesco De Nicola, Paola Castrucci, Manuela Scarselli, Francesca Nanni, Ilaria Cacciotti & Maurizio De Crescenzi, submitted to Thin Solid Films (2015).

The paper "Applications of three-dimensional carbon nanotube networks" has been presented also as invited paper at the fifth International Conference NanoSEA2014 (Marseille, France) by Manuela Scarselli.